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Osmium L_{III} edge extended X-ray absorption fine-structure studies on the osmium(VIII) oxide–fluorides, OsO_3F_2, $K[OsO_3F_3]$ and $Cs_2[OsO_4F_2]$

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Abstract

Osmium L_{III} edge extended X-ray absorption fine-structure data have been obtained for the title compounds and refined to give, for OsO_3F_2, $d(Os{=}O) = 1.70$ Å and $d(Os{-}F) = 1.89$ and 2.09 Å, for $K[OsO_3F_3]$, $d(Os{=}O) = 1.70$ Å and $d(Os{-}F) = 1.92$ Å and, for $Cs_2[OsO_4F_2]$, $d(Os{=}O) = 1.70$ Å and $d(Os{-}F) = 2.05$ Å (bond lengths accurate to ± 0.02 Å).

Introduction

Three oxide–fluoride species containing osmium(VIII) are well established: the orange trioxide difluoride OsO_3F_2, and two yellow anions $[OsO_4F_2]^{2-}$ and $[OsO_3F_3]^-$ [1–4]. A red $OsOF_6$ claimed very recently [5] is incompletely characterized[†]. In the gas phase, OsO_3F_2 is a trigonal bipyramidal monomer with D_{3h} symmetry [6, 7], but the solid is believed to be a fluorine-bridged polymer on the basis of its Raman spectrum [2]. Nguyen-Nghi and Bartlett [8] identified three different forms of the solid by X-ray powder diffraction studies, but the material has not been obtained as single crystals which would permit a full structural characterization. Similarly the anions in $M[OsO_3F_3]$ ($M{\equiv}K$, Rb or Cs) and $M'[OsO_4F_2]$ ($M'{\equiv}Rb$ or Cs) have been shown to have *fac* and *cis* geometries respectively on the basis of IR and Raman studies on the powders [4]. We have recently reported metal K or L_{III} edge extended X-ray absorption fine structure (EXAFS) data on a range of metal hexafluorides and fluoroanions [9, 10] and upon the monomeric oxide fluorides MnO_3F and CrO_2F_2 [11]. Here we report similar studies on the title compounds.

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[†] *Note added in proof*

The red material from the reaction of OsO_4 with the KrF_2 in anhydrous HF has now been definitively characterized as cis-OsO_2F_4 by IR, Raman and ^{19}F NMR spectroscopies and single-crystal X-ray analysis [19].

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Experimental

OsO_3F_2 was made by static fluorination of OsO_4 [2, 7], $K[OsO_3F_3]$ by heating together powdered OsO_3F_2 and KF [4], and $Cs_2[OsO_4F_2]$ by cooling a warm solution of OsO_4 in saturated aqueous CsF solution [4]. For EXAFS data collection, the moisture-stable $Cs_2[OsO_4F_2]$ was diluted with BN and run in a 1 mm aluminium holder between Sellotape strips. The highly moisture-sensitive OsO_3F_2 and $K[OsO_3F_3]$ were diluted with powdered LiF (BDH Ltd.) in a dry-box and loaded into the FEP (perfluoroethylene–propylene copolymer) cells described previously [9].

The EXAFS data were collected on station 7.1 at the Daresbury Synchrotron Radiation Source operating at 2 GeV with an average current of 190 mA. Data were collected in transmission mode using an order-sorting Si(111) monochromator. The osmium edge was calibrated using osmium powder in BN. Data treatment utilized the programs PAXAS [12] and EXCURVE90 [13]. Several data sets were collected on each compound, checked for the absence of anomalies and subsequently averaged. The pre-edge background was removed by fitting the spectrum to a cubic polynominal and subtracting this from the whole spectrum. The atomic contribution to the oscillatory part of the absorption spectrum was approximated using polynomials, and the optimum function judged by minimizing the intensity of chemically insignificant shells at low r in the Fourier transform. Curve fitting used single-scattering curved-wave theory with phase shifts and back scattering factors calculated using the normal *ab-initio* methods [13].

Results and discussion

The osmium edge EXAFS data on OsO_3F_2 were modelled to three shells of 3O, 1F and 2F consistent with fluorine-bridged structure (in which the osmium environment is $OsO_3F(\mu\text{-}F)_2$) suggested by the Raman spectrum. The best fit and its Fourier transform are shown in Fig. 1, and Table 1 contains the refined parameters. An alternative oxygen-bridged model (2O, 2F, 2O, environment $OsO_2F_2(\mu\text{-}O)_2$) was also investigated but gave a significantly worse fit (fit index, 2.53; $R = 26.5\%$), and the other refined parameters were also anomalous. Although the two models might be expected to be difficult to distinguish from the EXAFS, it seems that the major back scattering is provided by the terminal oxygen atoms at about 1.7 Å, and the poor fit of the oxygen-bridged model reflects the different occupation number of the first shell. There was no evidence in the Fourier transform for a remote osmium shell.

The $[OsO_3F_3]^-$ and $[OsO_4F_2]^{2-}$ anions were fitted to two shell models, and the best fits are given in Table 1. The oxygen atoms again dominate the back scattering, and this is evident in the high Debye–Waller factors of the second (fluorine) shells in each complex. In order to test the validity of the fits, the data for $[OsO_4F_2]^{2-}$ were fitted to a single shell of four oxygen atoms, which resulted in a similar $d(Os{=}O)$ of 1.70 Å but with an

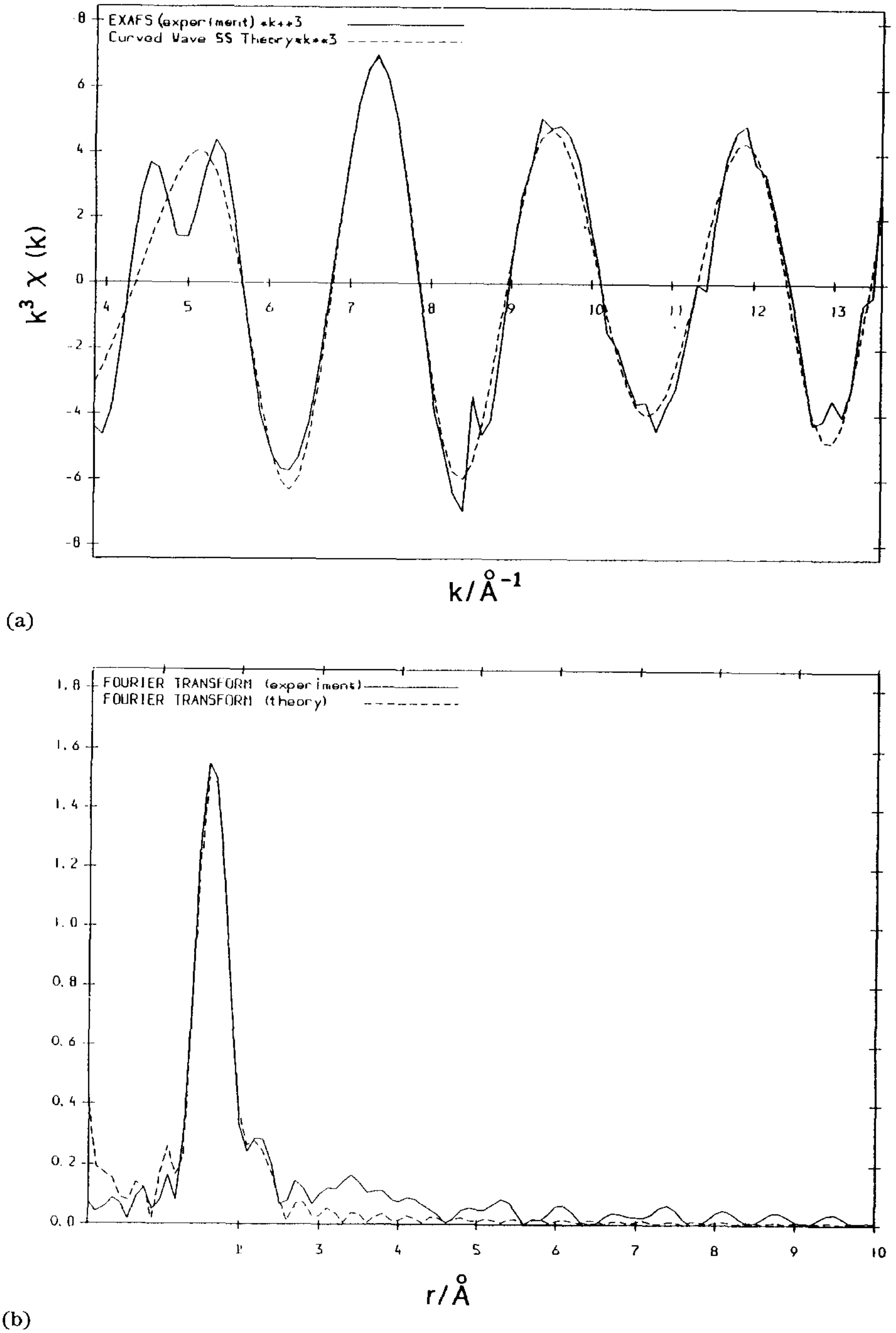

Fig. 1. (a) The background-subtracted EXAFS (κ^3 weighted) and (b) the Fourier transform for OsO_3F_2: ——, experimental data; – – –, calculated data.

TABLE 1

Refined extended X-ray absorption fine-structure data for osmium(VIII) compounds

	d(Os=O)[a] (Å)	$2\sigma^2$ [b] (Å^2)	d(Os–F) (Å)	$2\sigma^2$ (Å^2)	R[c]	Fit index[d]
OsO_3F_2	1.695(4)	0.0026(5)	1.885(11) 2.086(7)	0.0034(17) 0.0100(16)	17.61	1.64
$[OsO_3F_3]^-$	1.698(2)	0.0022(3)	1.919(15)	0.0435(55)	19.83	3.54
$[OsO_4F_2]^{2-}$	1.701(2)	0.0053(3)	2.048(29)	0.0486(90)	13.63	1.23

[a] Standard deviations are given in parentheses. Note that the systematic errors in bond distances arising from the data collection and analysis procedures are about 0.02 Å for well-defined coordination shells.

[b] $2\sigma^2$ is the Debye–Waller factor.

[c] The R factor is defined as $\{[\int(\chi^T-\chi^E)k^3\,dk]/\int(\chi^E k^3\,dk)\}\times 100\%$.

[d] The fit index is defined as $\Sigma_i[(\chi^T-\chi^E)k^3{}_i]^2$.

increase of 10% in the R factor. Thus we conclude that the two-shell fit is justified (and is consistent with the spectroscopic data).

For all three compounds the d(Os=O) is constant (within the present precision of EXAFS data which is about ±0.02 Å) at 1.70 Å, and may be compared with d(Os=O) in OsO_4 of 1.697 Å (mean) [14] and 1.76 Å (average) in the osmate(VIII) anions *cis*-$[OsO_4(OH)_2]^{2-}$ [15]. EXAFS determined the d(Os=O) in OsO_4 to be 1.69 Å [9]. There are no data in the literature on Os(VIII)–F bond lengths, but the values in Table 1 may be compared with the value of 1.82 Å in solid OsF_6 [9], and about 1.76 Å in $OsOF_5$ [16]. The longer d(Os–F) bond lengths in the osmium(VIII) complexes, are attributable to the dominant Os=O bonding, and the corresponding high *trans* influence of the oxygen atoms. The d(Os–F) in $[OsO_4F_2]^{2-}$ is about 0.1 Å longer than in the other two compounds, and this relatively weak Os–F interaction is reflected in the chemistry of the anion. For example the ion is largely dissociated in water unless a large excess of fluoride is present; the solid smells strongly of OsO_4 and completely loses OsO_4 on gentle heating [4, 17, 18]. In contrast the $M[OsO_3F_3]$ salts are thermally stable and are only partially decomposed on heating at 250 °C *in vacuo* [4].

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